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ABSTRACT

This paper contains discussions of several innovative thermal processes for treating or destroying hazardous wastes. Processes discussed can be included in the categories wet oxidation, molten glass, fluidized bed incineration, pyrolysis, molten salt, electric reactors, and plasma systems. The subject processes are among those new processes generating interest in the field of hazardous management technology. Information in this paper is from the USEPA report Innovative Thermal Hazardous Waste Treatment Processes prepared by the author in February, 1985.

INTRODUCTION

In recent years as individuals, organizations, and communities have become increasingly concerned about the disposal of untreated organic wastes directly into landfills, more attention has been given to thermal destruction processes as better solutions to hazardous waste management problems. Consequently, conventional thermal destruction processes such as rotary kilns, liquid injection incinerators, and multiple hearth incinerators are receiving much more consideration as hazardous waste management alternative technologies. Also receiving consideration as hazardous waste management alternatives are many new, or innovative thermal destruction processes. These processes, which differ in a variety of ways from conventional thermal processes, have been designed either to treat particular types of waste streams or to treat typical waste streams more effectively.

This paper contains discussions of nine such processes, as listed in Table 1. The intent of this paper is to provide overview information to those researchers and others involved with the management of hazardous wastes. Information for this paper was provided by the developers of the systems.

Wet Oxidation -- processes for oxidizing suspended and dissolved organics in aqueous waste streams. These processes are very effective at detoxifying aqueous waste streams that are too dilute to incinerate economically, yet too toxic to treat biologically. By confining the oxidation to the aqueous medium, wet oxidation does not produce the type or quantity of emissions produced by typical incinerators. The wet oxidation process using the feature of supercritical water is especially innovative in that effective separation of inorganics from the waste stream can be realized in addition to complete oxidation of organics. In general, it is a very promising alternative technology for a common hazardous waste stream, i.e., aqueous wastes containing non-chlorinated toxic organics. Commercial wet oxidation processes have been developed by the Zimpro Company and the MODAR Company.

TABLE 1. PROCESS SUMMARY

Process Name	Description	Waste Streams	For Information Contact
Zimpro Wet Air Oxidation	Uses elevated temperature and pressure to oxidize organics in water	Aqueous streams with less than 5% organics	William Copa Zimpro, Inc. Military Road Rothschild, WI 54474 (715) 359-7211
MODAR Supercritical Fluid Oxidation	Uses high temperatures and very high pressure to oxidize organic contaminants in water	Aqueous slurries or organic solutions	MODAR, Inc. 14 Tech Circle Natick, MA 01760 (617) 655-7741
Penberthy Electromelt Pyro Converter	Uses a bed of molten glass to oxidize organics and to capture ash and inorganics	Any liquid or solid waste stream	Penberthy Electromelt International, Inc. 631 South 96th Street Seattle, WA 98108 (206) 762-4244
Waste-Tech Services Low Temperature Fluid Bed	Uses granular combustion catalyst and limestone in a fluid bed	Liquids, sludges, slurries, or soils	Waste-Tech Services, Inc. P. O. Box 736 Idaho Falls, ID 83402 (208) 522-0850
Midland Ross Pyrolytic Decomposition	Heats waste materials in the absence of oxygen to drive off volatiles for incineration or recovery	Viscous liquids, sludges, and high ash materials	Midland-Ross Corporation Energy Technology Division 900 N. Westwood P. O. Box 985 Toledo, OH 43696 (419) 537-6444
Rockwell International Molten Salt Destruction	Uses a bed of molten sodium carbonate to destroy wastes and scrub acid gases	Low ash, low water content, solid or liquid wastes	Rockwell International Environmental and Energy Systems Division 8900 De Soto Avenue Canoga Park, CA 91304 (213) 700-8200
Huber Advanced Electric Reactor	Uses electrical heat to pyrolyze organic materials at extremely high temperatures	Finely ground solids	J. M. Huber Corporation P. O. Box 2831 Borger, TX 79007 (806) 274-6331
Pyrolysis Systems Pyroplasma	Uses plasma arc device to create extremely high temperatures for waste destruction	Highly toxic liquids	Pyrolysis Systems, Inc 4935 Kent Street Niagara Falls, Ontario L2H 1J6 Contact: Mr. Ian Thom
Applied Energetics Plasma Temperature Incinerator	Burns waste in a pressurized stream of preheated oxygen	Liquids and fluidized solid waste	Applied Energetics, Inc. P. O. Box 1177 Tullahoma, TN 37388 (615) 455-0631 Contact: Dr. John B. Dicks

Zimpro Wet Air Oxidation Process

The basic flow scheme of the Zimpro WAO system is shown in Figure 1. A wastewater stream containing oxidizable contaminants is pumped to the system pressure by means of a positive displacement-type pump. The wastewater passes through a heat exchanger which preheats the waste by indirect heat exchange with the hot oxidized effluent. The temperature of the incoming feed is increased to a level necessary to support the oxidation reaction in the reactor vessel. Air and the incoming liquid are injected into the reactor where the oxidation begins to take place. As oxidation progresses up through the reactor, the heat of combustion is liberated, increasing the temperature of the reaction mixture. This heat is recovered by interchanging with the incoming feed. Depending on the temperature of the oxidized effluent following interchange with the feed, final cooling may be required. After energy removal, the oxidized effluent, comprised mainly of water, carbon dioxide, and nitrogen is reduced in pressure through a specially designed automatic control valve.

Of all variables affecting wet air oxidation, temperature has the greatest effect on reaction rates. In most cases, about 150°C (300°F) is the lower limit for appreciable reaction, about 250°C (482°F) is needed for reaction to the 80-percent reduction of Chemical Oxygen Demand (COD) range, and at least 300°C (572°F) is needed for 95-percent reduction of COD or better reaction within practical reaction time.

Initial reaction rates and rates over the first 30 minutes are relatively fast. After about 60 minutes, rates become so slow that generally little increase in percent oxidation is gained in extended reaction.

WAO can reduce toxicant/contaminants to compounds such as H_2O, CO_2, and various simple acids, depending upon the waste in question. Specific toxic compounds such as the priority pollutants, phenols, cyanides, DDT, nitrosamines, and many carcinogens can be oxidized by WAO. The effluent liquor is suitable for either final discharge or is readily degradable if further biological treatmet is desired.

This process is available at commercial scale. The U.S. EPA and the State of California are supporting a demonstration of a 10 gal/min unit at Casmalia Resources near Santa Maria, California. Other units are operating on hazardous waste at Bofors Nobel in Muskegon, Michigan, and Northern Petrochemical Company in Morris, Illinois.

Modar Supercritical Water

The Modar supercritical fluid oxidation is basically a high temperature, high pressure wet oxidation. Above the critical temperature, 374°C (705°F) and pressure (218 atm) of water, organic meterials and gases are completely miscible with water. In supercritical water oxidation, organics, air, and water are brought together in a mixture at 250 atm and temperatures above 400°C (750°F). Organic oxidation is initiated spontaneously at these conditions. The heat of combustion is released within the fluid, and it results in a rise in temperature to 600°-650°C

(1100°-1200°F). Under these conditions, organics are destroyed rapidly with efficiencies in excess of 99.999 percent. Heteroatoms are oxidized to acids, which can be precipitated out as salts by addition of bases to the feed.

A schematic flowsheet for a Modar process for treating an aqueous waste containing 10 wt% organic is given in Figure 2. This process consists of the following steps.

1. The waste, as either an aqueous solution or a slurry, is pressurized and delivered to the oxidizer inlet. It is heated to supercritical conditions by direct mixing with recycled reactor effluent.

2. Oxygen is supplied in the form of compressed air, which is used as the motive fluid in an eductor to provide recycle of a portion of the reactor effluent. This inlet mixture is then a homogeneous phase of air, organics, and supercritical water.

3. The organics are oxidized in a controlled but rapid reaction. The short residence times that are required allow adiabatic operation of the oxidizer. The heat released by combustion of readily oxidized components is sufficient to raise the fluid base to temperatures at which all organics are oxidized rapidly.

4. The effluent from the oxidizer is fed to a cyclone. The solubility of inorganics in SCW is extremely low at the reactor effluent temperatures. Inorganic salts that are originally present in the feed, or which form in the combustion reactions, precipitate out of the fluid phase in the oxidizer and are separated here.

5. The fluid effluent of the solid separator consists of superheated SCW, N_2, and CO_2. A portion of this is recycled through the eductor to provide supercritical conditions at the oxidizer inlet.

6. The remainder of the effluent is available as a high-temperature, high-pressure fluid for energy recovery. This stream is cooled to a subcritical temperature in a heat exchanger which serves to generate low-pressure or high-pressure steam.

7. Now at a subcritical temperature, the mixture has formed two phases and enters a high-pressure liquid-vapor separator. Almost all of the N_2 and most of the CO_2 leaves with the gas stream. The liquid consists of water with an appreciable amount of dissolved CO_2.

8. The gas and liquid streams can then be expanded through turbines to extract the available energy as power. A portion of the power is used for compression of the inlet air.

9. The effluent from the liquid turbine enters a low-pressure separator. The vapor stream is primarily CO_2 which is vented with the gas turbine effluent. The liquid stream is clean water.

A 50-gallon per day pilot is under development to provide a verification of the laboratory-scale results.

Molten Glass -- processes that use a pool of molten glass as the heat transfer mechanism to destroy organics. The attractiveness of molten glass is based upon the extremely good quality of the residue from the process, i.e., essentially nonleachable glass. The combustion conditions for organics appear to be at least as good as those present in hazardous waste incinerators, and the inorganic residue and ash is incorporated into the glass. Introduction of this type of technology into the waste management industry, especially for highly toxic organic streams containing toxic metals, could prove very attractive if it can be shown through extraction tests that the residue is nonleachable and may be delistable as a hazardous waste.

Penberthy Electromelt System

Waste, both combustible and noncombustible, is charged onto a pool of molten glass in an electric furnace. The waste is burned to ashes (or dried to solids) which are immediately melted into the glass, all in the same chamber. Excess glass is drained off from time to time into canisters for ultimate disposal. The glass compositions used are very stable.

Referring to Figure 3, solid wastes, which can be in fiberboard boxes or loose, are pushed through the door opening into the glass furnace, which is heated electrically by immersed electrodes. Liquid and slurry wastes are introduced at a controlled rate through a pipe. If the liquid base is water, the water boils to steam progressively, leaving solids behind. If the liquid is oil, toluene, or other organics, the liquid burns to CO_2, H_2O, and HCl (if a chlorinated compound). Dirt and noncombustible content drop onto the glass and melt in. The gases go up through the filter to the spray chambers where the HCl is converted to common salt (NaCl).

The entire molten glass pool is kept above 2300°F (1260°C), which is well above the ignition temperature for combustible materials. These materials burn with admitted air in the first half of the chamber, while the second half of the same chamber "polishes" the process to insure complete combustion. Ashes and any noncombustible materials that drop onto the surface of the glass are melted into the glass. Wet, spent, ion-exchange resins first lose the water and then burn as above. Complementary raw materials, if needed, are charged into the furnace via a screw charger.

The flue gases pass through a set of ceramic fiber filters which catch substantially all of the particulate. When each filter in turn is loaded it is pushed into the furnace where it dissolves, capturing the dust into the glass. The flue gases then go through a gas-to-water heat exchanger and then to two water spray chambers. The first spray is held slightly alkaline to capture acidic gases. The water in the second chamber is

fairly pure to prevent loaded water from passing onward into the rest of the system. The demist chamber takes out practically all of the droplets. The gases are then reheated above the dewpoint. The gases then pass through charcoal and HEPA filters before going to the blower and out of the vent stack.

Filter sludge from the spray chambers and the charcoal and HEPA filters are disposed of in the furnace. The charcoal burns to carbon dioxide and the dust and smudges are melted into the glass. HEPA filters (no metal parts) melt into the glass pool, capturing their contained dust.

The glass is tapped off from time to time as necessary into canisters. After cooling, the canisters are ready for final disposal.

The entire system is maintained under negative pressure by means of the exhaust blower. Combustion air is admitted to the furnace through ports which control oxygen as desired, usually 4 pecent minimum for completeness of combustion.

The technology is offered commercially. The Pyro-Converter is sold as chemical processing equipment, not as an incinerator. Smaller units are available for in-plant use. Larger units are available for use by disposal companies.

Fluidized-Bed Incineration -- thermal processes using a very turbulent bed of inert granular material to improve the transfer of heat to the waste streams to be incinerated. Advantages of fluidized-bed incinerators include their relatively compact design, their relative simplicity of operation, and their ability for combining combustion with pollution control by trapping some gases in the bed. Although fluidized beds have been used for many years in various industries, their use in hazardous waste incineration is still at a demonstration level. It is generally agreed, however, that this approach to waste incineration offers significant potential for the future.

Waste-Tech Process

The heart of this system is a fluidized bed, operating at low temperatures, and composed of a mixture of a granular combustion catalyst and limestone. Liquid waste, sludge, or granular solids (with fuel oil as needed) are metered into a pneumatic injection tube which injects the stream into the bottom of the bed. Fluidizing air is forced up through this bed at a high enough velocity such that the bed behaves much like a boiling liquid. Limestone is continuously added to the bed. Bed material is periodically drained from the vessel. Particulate removal is in the form of a multiclone system with final flue gas cleanup in a baghouse or other high-efficiency collection system.

Preliminary data suggest that the technology may offer an economic advantage over other systems due to lower operating temperatures, reduced fuel oil requirements, and ability to use standard materials in construction. To date, however, no complete process economics are available.

High temperature fluidized beds, 925°-1200°C (1700°-2200°F), are offered or used where the use of catalytic beds is uneconomical or inefficient.

The unit is offered commercially either as a service with Waste-Tech Services owning and operating units, or as a turnkey system.

Pyrolysis -- processes that break down waste materials into less complex materials through the application of heat in the absence of oxygen. Pyro-conversion units are typically custom designed to process specific types of chemicals rather than as multipurpose waste processing units. Consequently, their use as multipurpose hazardous waste treatment facilities has been very limited. However, pyrolysis processes can be designed for use as a multipurpose waste processing units. Advantages of pyrolysis processes are that there is a potential for byproduct recovery, that sludge volumes may be reduced without large amounts of supplementry fuel being used, and that air emissions are usually less than for conventional incinerators.

Well-known examples of pyrolysis processes are the Midland-Ross Corporation's pyrolytic decomposition systems, Pyrotherm and Pyrobatch.

Midland Ross Pyrolysis Systems

The pyrolytic incineration system is designed for granular or liquid materials and includes three major components: a continuous feed furnace, rich fume reactor, and heat recovery device. The furnace is fashioned after high-temperature furnaces used for treating metals and other materials requiring controlled thermal treatment. Waste is continuously fed and passes into an indirect-fired, oxygen-free, pyroytic chamber. There, the waste is heated to between 540°C (1000°F) and 870°C (1600°F) depending on the type and amount of inert materials in the waste. The heat drives off all volatile components leaving behind the inert materials, and pyrolysis of the waste is normally accomplished in a 15- to 30-minute period of time.

Any remaining inert residue (char) is continuously removed and more feed material is continuously fed into the PyroTherm® furnace. The energy-bearing gaseous fraction then is completely combusted in the rich fume reactor, and the resulting hot gases enter a boiler or other heat recovery device to efficiently recover waste as a usable energy source.

The PyroBatch system is designed primarily to treat liquids, solids, or semisolids in 55-gallon drums. This type of system consists normally of a batch furnace, a rich fume reactor, and a heat recovery device (if desired). One such system was RCRA permitted in 1984 at McDonnell Douglas Company in St. Charles, Missouri. It is the first "New Hazardous Waste Incinerator" in Region VII U. S. EPA and the State of Missouri.

Pyrolytic incineration is for processing materials that fall into the following categories:

1. Too viscous to atomize in liquid incinerators, yet too fluid for spreader-stoker incinerators.

2. Low melting point materials that foul heat exchangers, spall refractories, and complicate residue discharge.

3. High residue materials (ash), with easily entrained solids, that would generally require substantial stack gas cleanup.

4. Material containing priority pollutants with excessive vapor pressure at incineration temperatures.

5. Any material, drummed or loose bulk, where controlled thermal treatment is desired to make clean gases for heat recovery or for discharge to the atmosphere.

PyroBatch® systems are available from 2-drum to 20-drum capacity and are prepiped and wired, skid-mounted, shop-bricked modules available for quick delivery and easy assembly.

MOLTEN SALT

Molten salt -- a process in which waste material is injected beneath a bed of molten sodium carbonate for incineration. The process is innovative in that the use of the molten bed requires lower temperatures for waste combustion. Also, the bed acts as a very effective scrubbing medium for acid gases.

Rockwell Molten Salt Process

A molten salt process has been developed by the Rockwell International Company. The process consists of injecting the material to be burned with air, or oxygen-enriched air, under the surface of a pool of molten sodium carbonate. The melt is maintained at temperatures on the order of 900°C (1650°F) causing the hydrocarbons of the organic matter to be immediately oxidized to carbon dioxide and water. The combustion by-products containing such elements as phosphorus, sulfur, arsenic, and the halogens react with the sodium carbonate. These byproducts are retained in the melt as inorganic salts rather than released to the atmosphere as volatile gases. In time, inorganic products resulting from the reaction of organic halogens, phosphorus, sulfur, etc., build up and must be removed from the molten bed to retain its ability to absorb acidic gases. Ash introduced by the waste must be removed to preserve the fluidity of the melt. An ash concentration in the melt of about 20 percent by weight provides an ample margin of safety to maintain melt fluidity. Melt removal can be done continuously or batchwise.

Depending upon the size and design application of the particular unit, the salt in the bed is recovered or disposed of when it becomes excessively laden with ash or products of acid gas reaction. The process can operate at atmospheric pressure or elevated pressure (see Figure 5).

Rockwell is currently engaged in discussions with potential licensees with regard to demonstration and commercialization of the process.

Electric Reactor -- processes that pyrolyze waste contaminants off particles such as soil through use of an electrically heated fluid wall reactor. These units have been used successfully in other chemical processes and are just beginning to be adopted for waste destruction. The units, especially the portable versions of the processes, appear to offer a very different and potentially valuable thermal option for hazardous waste treatment.

The Huber Technology Group, Borger, Texas, has developed a waste treatment process that uses a high temperature electric reactor.

Advanced Electric Reactor - Huber

The Huber Technology Group (HTG) process is based on the Advanced Electric Reactor (AER) which is shown in Figure 6. The reactor employs a new technology to rapidly heat materials to temperatures in the range of 4000°F using intense thermal radiation in the near-infrared region. The reactants, which can be in gaseous, liquid, or solid form, are isolated from the reactor core walls by means of a gaseous blanket formed by flowing nitrogen radially inward through the porous core walls. Carbon electrodes are heated and in turn heat the reactor core to incandescence so that heat transfer is accomplished by thermal radiative coupling from the core to the feed materials. The only feed streams to the reactor are the solid, liquid, or gaseous wastes and the blanket gas, nitrogen. Destruction is accomplished by pyrolysis rather than oxidation. Therefore, typical products produced by incineration, such as carbon monoxide, carbon dioxide, and oxides of nitrogen, are not formed in significant concentrations. The principal products of soil-borne PCB destruction using the Huber process are H_2, Cl_2, HCl, elemental carbon, and a granular, free-flowing, solid-derived material. For solid waste treatment, the solid feed stream is introduced at the top of the reactor by means of a metered screw feeder connecting the air-tight feed hopper to the reactor. Nitrogen is introduced primarily at two points in the reactor annulus formed by the external containing vessel and the porous graphite core which creates the fluid wall. The solid feed passes through the reactor where pyrolysis occurs at temperatures above 2200°C (4000°F). After leaving the reactor, the product gas and waste solids pass through two post-reactor treatment zones (PRTZ). The first PRTZ is an insulated vessel to provide additional high temperature (in excess of 1100°C, 2000°F) and residence time (5 to 10 seconds) while the second PRTZ is water-cooled. It also provides additional residence time (approximately 10 seconds) but primarily cools the gas to less than 540°C (1000°F) prior to downstream particulate cleanup.

Huber maintains two fully equipped Advanced Electric Reactors in Borger, Texas, as part of an over $4 million AER pilot facility. The smaller reactor, which has a nominal core diameter of 3 inches, is used for proof-of-concept experiments. The larger reactor, which is of commerical

scale, has a 12-inch core diameter but is used primarily for research purposes.

It is anticipated that by the second quarter of 1985 Huber will have a transportable 20,000 to 30,000 ton per year unit ready for the demonstration of treating dioxin-contaminated soil. A 50,000 ton per year unit can be available in early 1986 if applications are identified.

Plasma Systems -- processes that use the extremely high temperature of plasma to destroy waste materials. The plasma systems offer a very innovative approach to destroying highly toxic chemicals. Several systems have been reserched. Two of these systems are discussed in this paper.

The Pyroplasma Process

In this plasma arc device, a co-linear electrode arrangement creates an electric arc which is stabilized by field coil medium through which an electric current is passed. As air passes the arc, the electrical energy is converted to thermal energy by adsorption by the air molecules which are activated into ionized atomic states, losing electrons in the process. Ultraviolet radiation is emitted when the molecules or atoms relax from their highly activated states to lower energy levels.

The resulting gas is in the plasma state consisting of charged and neutral particles with an overall charge near zero and with electron temperatures up to 28,000°C (50,000°F). As the activated components of the plasma decay, their energy is transferred to the waste materials exposed to the plasma; the wastes are ultimately decayed and destroyed.

A schematic of this process is shown in Figure 7.

The testing of this technology has been the subject of continuing support support from the EPA and the New York Department of Environmental Conservation. The fabrication of mobile unit capable of treating from 1 to 2 gallons per minute of waste was completed in the spring of 1984. A four-stage demonstration of this mobile unit is currently underway in Kingston, Ontario.

Applied Energetics Process

This incinerator burns the toxic waste including PCB in a pressurized stream of preheated oxygen. The operation can achieve temperatures of 2760°C (5000°F) and maintain them at elevated levels for periods of up to 1 second. Figure 8 illustrates the major components of a stand-alone incinerator that is designed for a feed rate of 1900 liters per hour.

This plasma-incinerator system, as shown in Figure 8, contains a preheater, a combustion chamber, a reaction residence chamber, a quench chamber, a scrubber tower, and an exhaust stack. The preheater is a refractory-lined, water-cooled chamber in which a clean fuel is burned

to preheat oxygen to about 1000°C (1800°F). The preheater consumes fuel at the rate of 120 kg/h to preheat 4.5 metric tons per hour of oxygen. The preheated oxygen enters the combustion chamber through a disperser plate. The disperser plate contains a number of fuel nozzles and oxygen ports, and it is designed to achieve optimal mixing of the two reactants. The temperature of the prehated oxygen is sufficient to auto-ignite any fuel when the heat of combustion is at least 14 kJ/g. This arrangement minimizes the risk of flameout and subsequent contamination of the area with partially-burned toxic waste.

A prototype of this system has been tested by a commercial waste treatment firm and performed to destroy PCB to within EPA standards.

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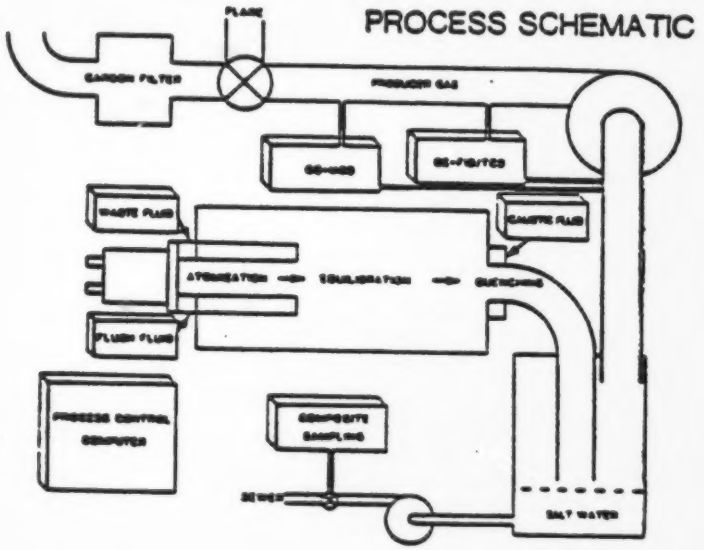


Figure 7 Pyroplasma process schematic.

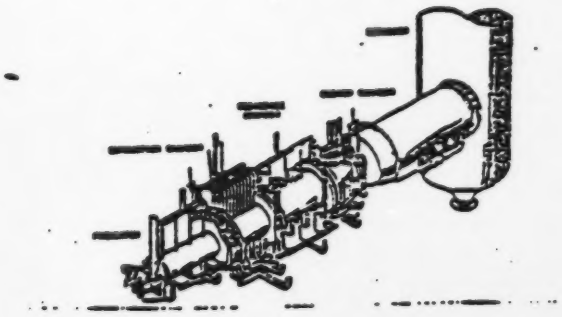


Figure 8 Plasma temperature incinerator.

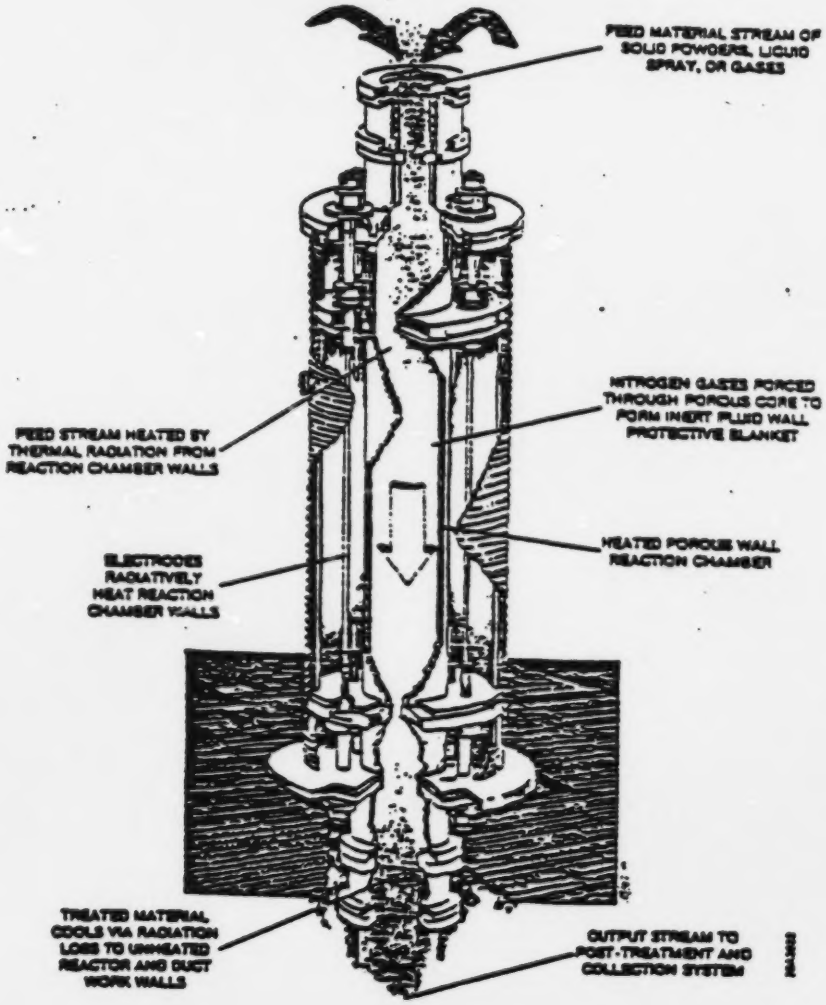
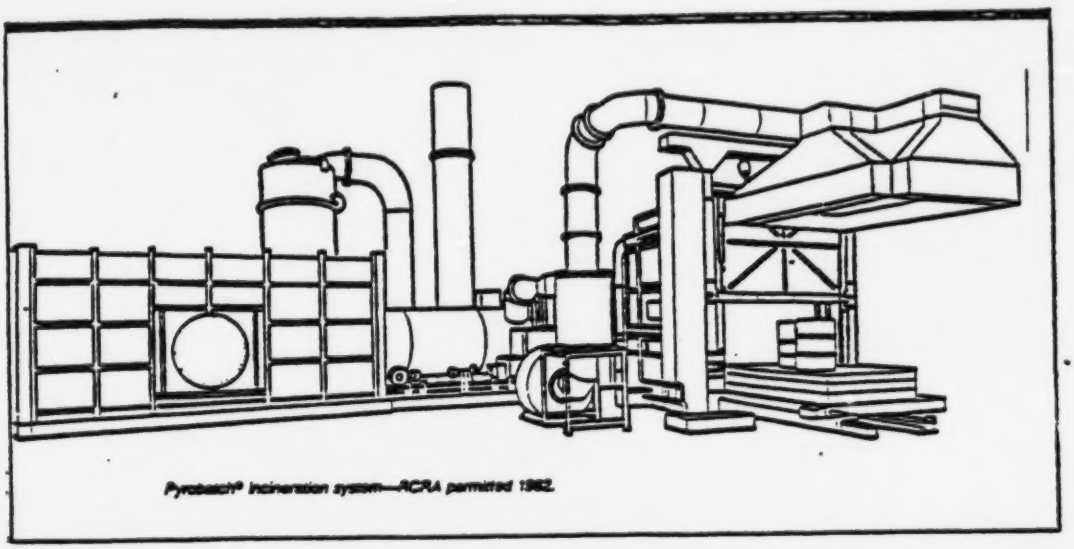

FEED MATERIAL STREAM OF SOLID POWDERS, LIQUID SPRAY, OR GASES
NITROGEN GASES FORCED THROUGH POROUS CORE TO FORM INERT FILLED WALL PROTECTIVE BLANKET
FEED STREAM HEATED BY THERMAL RADIATION FROM REACTION CHAMBER WALLS
HEATED POROUS WALL REACTION CHAMBER
ELECTRODES RADIATIVELY HEAT REACTION CHAMBER WALLS
TREATED MATERIAL COOLS VIA RADIATION LOSS TO UNHEATED REACTOR AND DUCT WORK WALLS
OUTPUT STREAM TO POST-TREATMENT AND COLLECTION SYSTEM

Figure 6 Advanced electric reactor.



Pyrobatch® incineration system—RCRA permitted 1982.

Figure 4 PyroBatch® illustration.

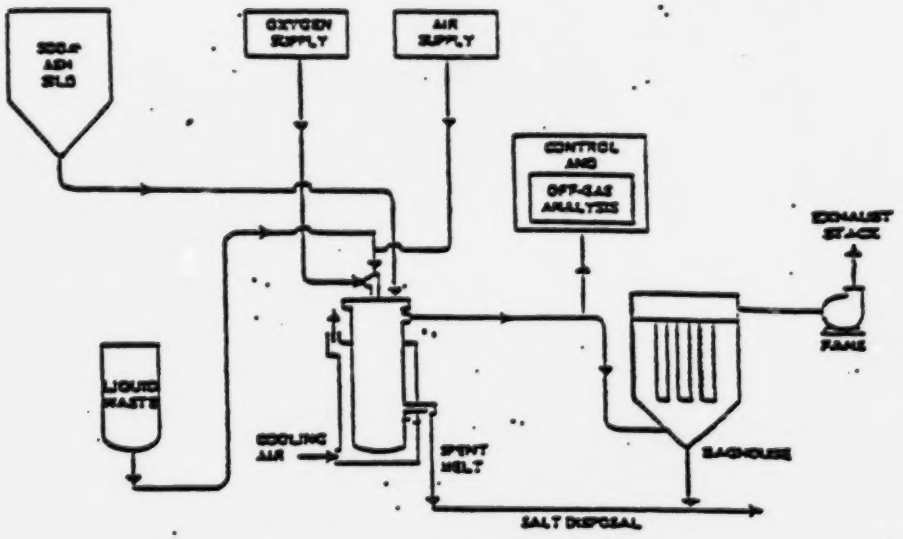


Figure 5 Simplified diagram of the molten salt waste destruction process.

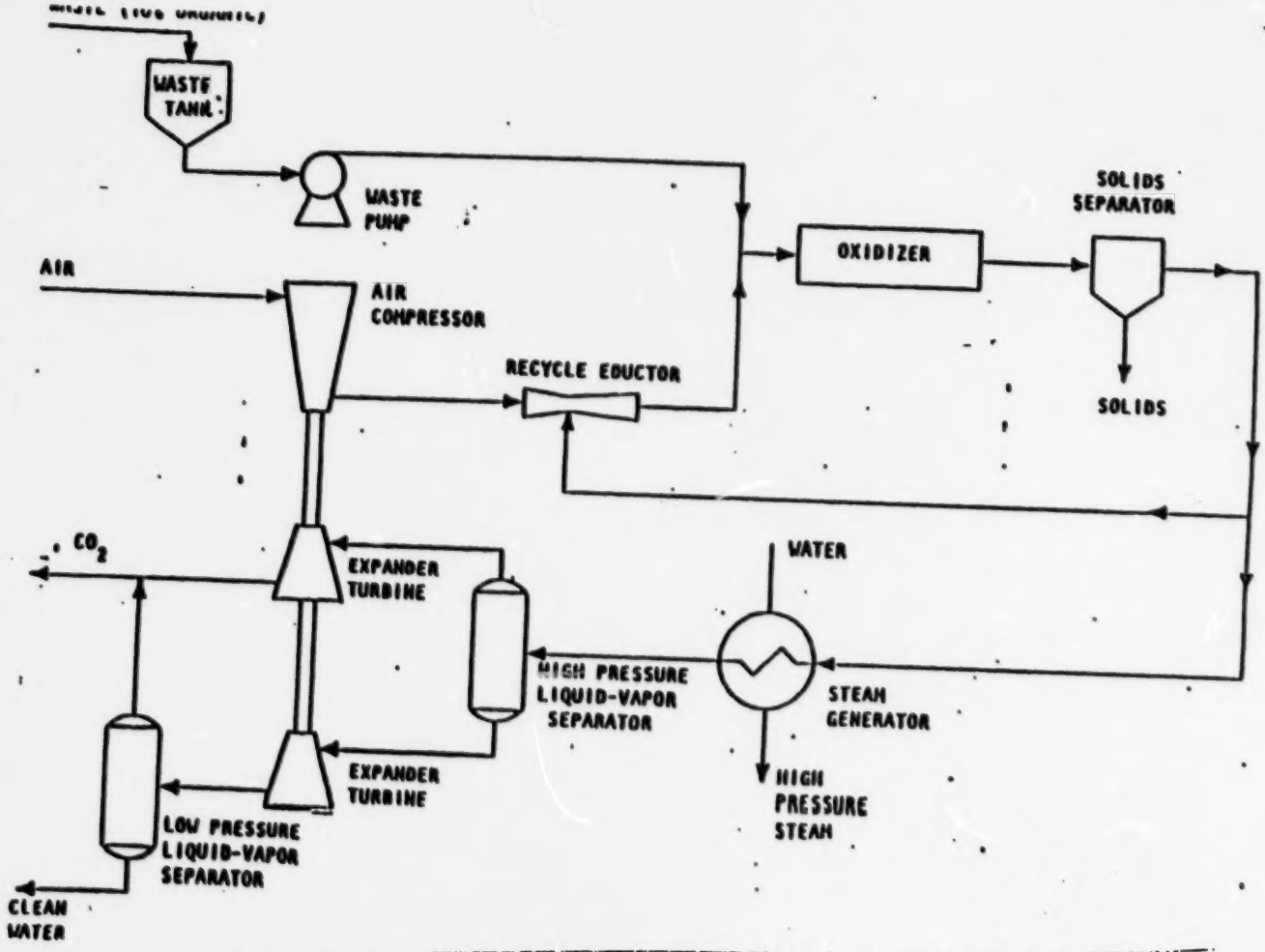


Figure 2 Process schematic for oxidation of an aqueous waste with a heating value of 1750 Btu/lb.

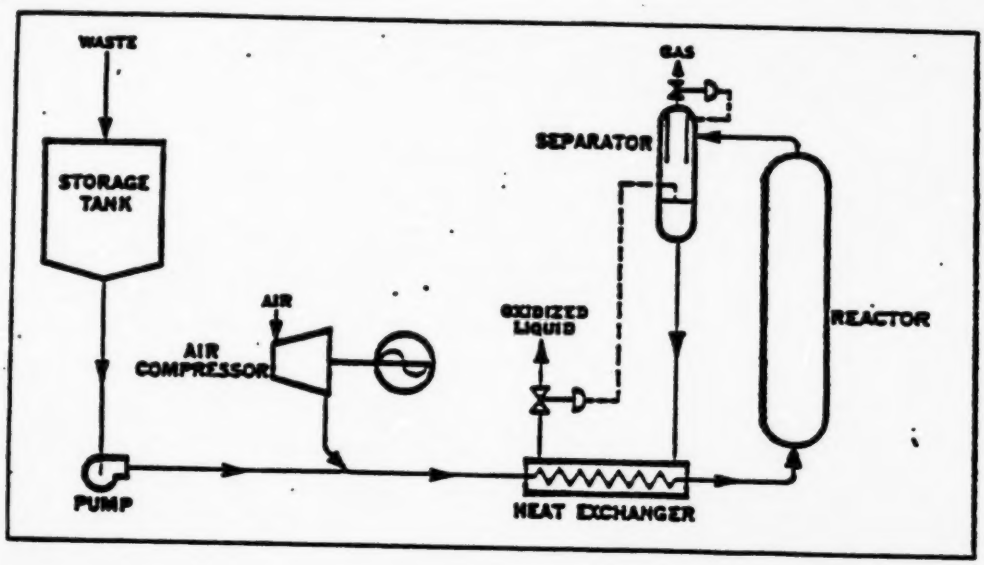


Figure 1 Flowsheet of wet air oxidation process.

Penberthy PYRO-CONVERTER™

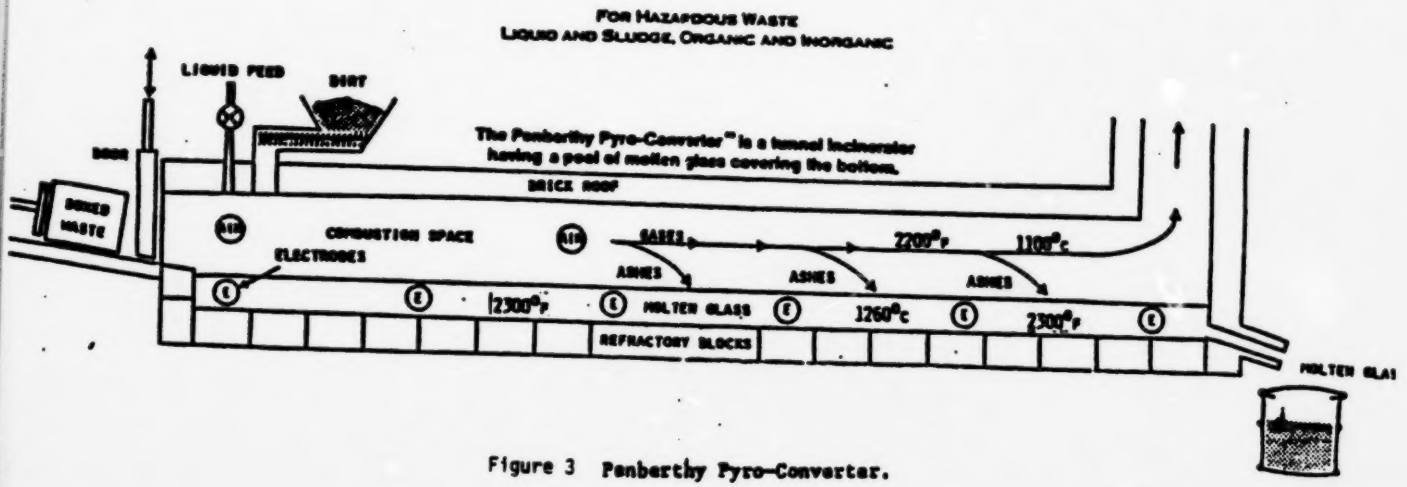


Figure 3 Penberthy Pyro-Converter.